FAP #5H1740

Petitions Control Branch and
Division of Toxicological Evaluation

October 19, 1966

AF 24-806

Pesticides Branch, Division of Food
Standards and Additives

FAP #5H1740. Residues on cereal milling fractions from use of piperonyl butoxide pyrethrins sprays. Evaluation of analytical methods and residue data

West Chemical Products Inc., proposes to amend Sec. 121.1074 and 121.1075 to permit the use, in mills and milled cereal product storage areas, of synergized pyrethrins with piperonyl butoxide to pyrethrins ratios varying from 1:1 to 10:1. (10:1 is approved at present). No change is proposed in present tolerances of 10 ppm for piperonyl butoxide and 1 ppm for pyrethrins in milling fractions derived from cereal grains.

The petitioner claims that amending the regulations in this manner would facilitate the use of more effective formulations against crawling insects. PRD, USDA (see letter of 2/18/65 from J. Ward to P.B. Bartlett) has indicated that no question of efficacy would be raised so long as the formulations contained at least 0.1% pyrethrins and the ratio of piperonyl butoxide to pyrethrins was at least 1:1.

Conclusions

1. Adequate methods are available to enforce the present tolerances which remain unchanged under the proposed amended regulations.

2. Residues from the present and amended uses would not exceed the present tolerances of 10 ppm for piperonyl butoxide and 1 ppm for pyrethrins.

Recommendation

Pharmacological considerations permitting, we recommend that the proposed amendment permitting piperonyl butoxide to pyrethrins ratios of 1:1 to 10:1 be adopted.

Note: In the past we have relied on the approved 10:1 ratio as an expedient for the control of pyrethrin residues. Lacking an adequate method for pyrethrin residues, the method for piperonyl butoxide residues was available to enforce the tolerances for both spray components. (Piperonyl butoxide

being the more stable, the pyrethrin residue levels were assumed to be always 10% or less of those of piperonyl butoxide. This assumption has now been validated by the data in this petition). This expedient would no longer apply if the proposed range of ratios were to be permitted.

However the proposed use would not yield residues of pyrethrins in excess of the present 1 ppm tolerance. Residues of piperonyl butoxide would be even lower than under the present regulation. Moreover the high cost of pyrethrins would militate against the over use of this material.

## Detailed Considerations

### Use

The petitioner's supplement of 11/3/65 contains a label for "Pyrosect", the formulation for flour mill use, which is similar to the one submitted on 6/2/65 except for an additional use involving surface sprays. Our evaluation is based on the label of 11/3/65.

The "Pyrosect" formulation contains 0.25% piperonyl butoxide and 0.1% pyrethri (i.e. in the ratio of 2.5:1). It is to be fogged at a rate of 1 pt/5000 cu. ft. for flying insects and 1 qt./5000 cu. ft. for crawling insects. In addition walls, floors and other accessible surfaces are to be sprayed at a rate of 1 gal./750 sq. ft. In the latter use, dust, debris and waste farinaceous material are to be cleaned out before application.

In his letter of 6/2/65 the petitioner stated that the maximum dosage was that given on the label. In addition no new formulations are anticipated at this time.

### Residue Methods

Piperonyl butoxide After extraction and cleanup, samples are analyzed by the TLC method of Beroza (see J. Ag. Food Chem., 11, 51; 1963). Although essentially a qualitative procedure, the method has been made quantitative by using a densitometer to compare the intensity of the spots developed with those obtained from standards.

While the blanks are reported as zero we consider 0.02 ppm to be the practical limit of sensitivity based on data in the 12/1/65 letter from Mr. G. J. Baker. Data show lowest recoveries including one value of 40% at the lowest fortification levels but this improved with increased fortification. The recoveries on flour samples fortified with 0.05-1.0 ppm range from 60-100%. The sensitivity is satisfactory in relation to the existing tolerance for the piperonyl butoxide component.

The petitioner also used an electron capture GLC method for some check analyses. This method hopefully will prove adequate eventually for enforcement use but requires further investigation. However, should the need ever arise, we would expect the colorimetric AOAC procedure based on the chromotropic acid reaction with formaldehyde (see "Pesticide Manual" Vol. II) to be the method of choice.

Pyrethrins The method for pyrethrins is based on electron capture GLC and involves the use of a special detector devised by W.N. Bruce of the Illinois Natural History Survey. The determinative step entails measuring the peaks due to pyrethrin I & II and cinerins I & II. At low concentrations the peaks due to pyrethrin I and cinerin I may be obscured by interfering materials in flour; but as little as 0.02 ppm of pyrethrins can be detected by using the pyrethrin II and cinerin II peaks. Recoveries on flour samples fortified with 0.05-0.5 ppm range from 85-100%. The sensitivity is satisfactory in relation to the existing tolerance for the pyrethrins component.

Using the above method would require the use of the special detector devised by W.N. Bruce. However, pyrethrins have been analyzed by a similar procedure without cleanup (see letter of Mr. G.J. Baker, 12/16/63 in FAP #404). These data indicate that at least 1.7 ppm of pyrethrins can be determined using conventional GLC equipment. Hence we would expect that further investigation of this method would eventually yield a procedure adequate for enforcing the 1 ppm tolerance without the use of the special detector.

General Considering the relatively innocuous nature of the pesticides we would expect little if any enforcement action on these tolerances and no method tryout is necessary.

Residue Data

In the residue study 3 lb samples of flour and the inert diluent, Pyrax ABB in sealed, 2-ply Kraft paper bags and open 1 gal. glass battery jars were placed in a 100-cu. ft. chamber. Half of the jars were uncovered and half had lids raised 1/2" to simulate flour protected from direct fall out. The chambers were fogged at a rate of 0.8 oz/100 cu. ft. with the presently approved 10:1 formulation (1% piperonyl butoxide and 0.1% pyrethrins)-- and at rates of 0.2 and 0.4 oz/100 cu. ft. with a 1.25:1 formulation containing 0.5% piperonyl butoxide and 0.4% pyrethrins. These formulations bracket the 2.5:1 Pyrosect formulation which is that being proposed for use at this time. Twenty-four hours later, surface samples were taken for analysis. For two treatments, the samples involved were left in the chambers for 1 week between foggings.

Residues from this test will exceed those obtained in actual practice. The samples were kept in small containers with high surface to volume (and weight) ratios, the aliquots analyzed represented surface (rather than composite) residues, and the fogging was done in a small air-tight chamber with little or no loss of pesticide. In addition the rates are somewhat in excess of those proposed for the Pyrosect formulation.

In regard to the frequency and number of applications, M. Prochaska of FAB, FSA informs us that mills are unlikely to be treated more than once a week. Further any particular batch of grain fractions is unlikely to remain in the mill long enough to be exposed to more than 2 sprayings.

Overall we consider this study a reasonably conservative reflection of the residues likely to result from the proposed use of the Pyrosect formulation.

The residue data on bagged flour and Pyrax ABB show very low residues of each spray component ranging from 0.00-0.03 ppm--practically within the 0.02 ppm sensitivities. For surface samples from jars with 1 or 2 treatments at rates equivalent up to 2.5 times that presently proposed for pyrethrins, the range of pyrethrins residues is 0.00-0.48 ppm--and the range of piperonyl butoxide residues is 0.03-1.61 ppm.(The highest values being for the 10:1 formulation). These values are well below the tolerance levels of 1 ppm for pyrethrins and 10 ppm for piperonyl butoxide.

The above study is supported by a similar study, with formulations including MGK264, reported in FAP #404. There pyrethrins and piperonyl butoxide residues, where treatments are comparable, are of the same order of magnitude as in the above study. While the 1 gal/750 sq. ft. spray treatments were not reflected, these are primarily for surfaces that do not come in contact with flour. (There is a label requirement that equipment be cleaned before treatment.) In addition there are data elsewhere on the presently approved 10:1 formulation (discussed below) which reflect the surface treatments.

These studies are reinforced by data obtained in a flour mill in support of the original regulation [see FSA (J.Alpert) memo of 9/21/61 in FAP #422]. The data include residue values reflecting surface applications and are also pertinent to the proposed use. Under some conditions residues exceed those in the above studies, but still are below the existing tolerance level for piperonyl butoxide. (The highest residue, 8 ppm of piperonyl butoxide was obtained on a flour 'spill' sample which was placed on freshly treated wood flooring.)

If at some future time, the petitioner registers labels with other ratios of piperonyl butoxide to pyrethrins, the controlling feature would be the rate of pyrethrins application. Since this is a relatively expensive component, economic considerations would preclude the use of more than is required. Thus even though the concentration of pyrethrins in the formulation may be higher than it is at present, the rate would be correspondingly reduced. Under these conditions residues of piperonyl butoxide would be less with the 1:1 ratio than they are with the current 10:1 ratio.

Therefore, we conclude that residues from the amended use will not exceed the existing tolerances of 10 ppm for piperonyl butoxide and 1 ppm for pyrethrins.

Other Considerations

Although the residue methods were not validated for grain fractions other than flour, data in FAP #6H1946 show adequate recoveries when the methods are applied to a wide variety of substrates.

The unavoidable comingling of materials in flour mills would result in residue dilution when treated materials are mixed with those which have not been exposed to pesticides. In addition the heating of milling fractions in the preparation of food (e.g. baking) would reduce, any residues present.

Since the proposed amendment would not result in increased tolerances, no problems on the transfer of residues to meat and milk are presented.

J. Wolff

cc:

DTE
SCI-OD
SCI-R
FSA/OD
FSA/PB
FAP #4Q4
FAP #422
FAP #5H1740
FAP #6H1946
DFC(Jones)
SCI(Johnson)

JWolff:dep 10/19/66

RD/I--JAlpert:GJBeusch

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